THE HEAT OF ABSORPTION AT 0° OF SULPHUR DIOXIDE AND WATER VAPOR BY SILICA GEL.

THE HEAT OF OXIDATION AT 0° OF CARBON MONOXIDE AND HYDROGEN BY MANGANESE DIOXIDE.

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BY

CLARENCE E. GREIDER

DISSERTATION

Submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

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HEATS OF ADSORPTION OF SULFUR DIOXIDE AND OF WATER VAPOR BY SILICA GEL AT 0°C*

BY W. A. PATRICK AND C. E. GREIDER

Heats of adsorption from the gas phase have been measured by a number of previous workers including Favre[1], Titoff[2], and Lamb and Coolidge[3]. In each case note is made of the fact that the heat of adsorption is greater per gram of vapor adsorbed than the corresponding heat of liquefaction at the temperature. Since it is assumed that the vapor is liquefied in the pores or on the surface of the adsorbent, various explanations have been advanced to account for the difference between the heat of adsorption and the heat of liquefaction. This difference should at saturation be equal to the heat of wetting, and is called by Lamb the net heat of adsorption. He assumes that this "net heat" is due to compression of the adsorbed liquid by the forces of molecular attraction, and from this he calculates that in the cases with which he worked the adsorbed liquid was under a pressure of about twenty thousand atmospheres.

Harkins and Ewing[4] have suggested that the heat of wetting, which they call the heat of spreading, is due to the change in surface energy involved, and derive equations to express their ideas, but do not attempt any quantitative calculations.

Recent work in this laboratory[5] has shown that, when silica gel is used as the adsorbent, it is possible to calculate quantitatively the heat of wetting from changes in surface energy. The most active samples of silica gel, activated by heating at 250°-300° in vacuo for a half hour or more, contain from three to six percent of water. It is therefore assumed that the gel before wetting exhibits a water surface. Wetting by water would therefore simply fill up the pores of the gel and reduce the water surface from its original very large value to practically zero. The heat of wetting of silica gel by water was measured at 25°, and the specific surface of the gel calculated on the assumption that the heat measured was due entirely to liberation of the total surface energy of the water. The specific surface obtained in this way agreed very well with that obtained from ultramicroscopic investigations.

The purpose of this work was to measure heats of adsorption at 0°, with silica gel as the adsorbent. In the adsorption of water vapor at 0°, the net heat of adsorption should be negative if it is due to compression of the adsorbed water. If, on the other hand, the net heat is due entirely to liberation of surface energy, it should at saturation be equal to the heat of wetting as

* Contribution from the Chemical Laboratory of Johns Hopkins University.

[1] Ann. Chim. Phys. (5) 1, 209 (1874).

[2] Z. physik. Chem. 74, 641 (1910).

[3] J. Am. Chem. Soc. 42, 1146 (1920).

[4] Proc. Nat. Acad. Sci. 6, 49 (1920).

[5] Patrick and Grimm: J. Am. Chem. Soc. 43, 2144 (1921).

measured at 25°, since the total surface energy of a liquid is, within the temperature limits under consideration (0° − 25°) independent of the temperature.

Apparatus

The system shown in Figs. 1 and 2 was used for all heat measurements at 0°. In Fig. 1, A leads from the first mercury trap to the vacuum line. Evacuation was produced by a Gaede mercury pump and a Hyvac oil pump in series. B is a McLeod gauge, C a second mercury trap, and D a three-way mercury sealed stopcock. G is a cooling coil surrounded with ice and water, and H a ground-glass joint connecting the adsorption bulb I with the remainder of the system.

If this system is evacuated to less than 0.001 mm. pressure for two successive days—the second evacuation to remove gas set free from the glass walls—it will hold the pressure below this point for at least a week.

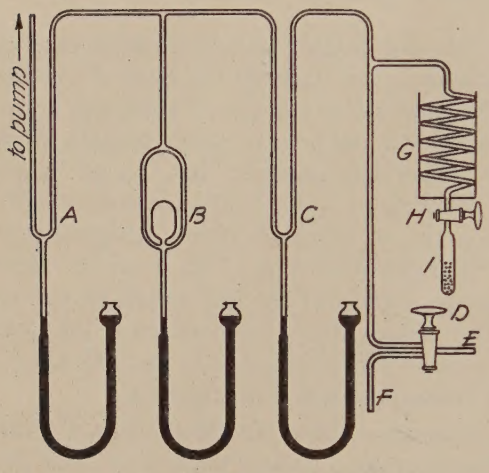

FIG. 1

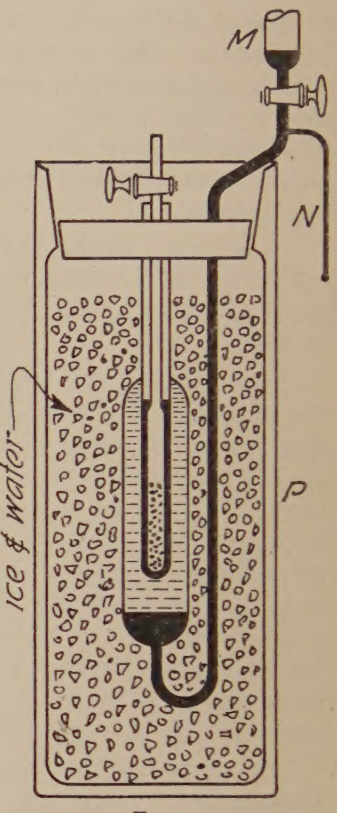

FIG. 2

The measurements of heat at this temperature were made with a modified Bunsen ice calorimeter, as shown in Fig. 2. M is a mercury reservoir, and N a capillary tube ending in a tip of the shape recommended by Ostwald and Luther.[1] The heat given off (or absorbed) is followed by the change in weight of small mercury cups placed under the tip of N. The inner tube of the calorimeter has in it sufficient mercury to stand to about the height shown in the figure, in order that thermal equilibrium between the adsorption bulb and the calorimeter might be more quickly attained.

[1] "Physiko-chemische Messungen," 3d Ed. p. 332 (1910).

The calorimeter is placed in a two quart "Ferrostat" vacuum jar, filled with a mixture of ice and water. It was found that ordinary ice if well washed would keep the temperature at such a point that heat interchange between the calorimeter and its surroundings was negligible. This blank was, however, re-determined at each filling.

Materials

The mercury and the rubber connections were cleaned in the usual manner. The sulfur dioxide was taken from a tank of the commercial material, from which the first portions were allowed to escape. It was dried by passage through a U-tube filled with phosphorus pentoxide. The silica gel was prepared by the process used by Patrick and McGavack[1] and when dried for two hours at 300°, various preparations contained from 3.5 to 5.5 percent of water.

Procedure

In the adsorption of sulfur dioxide the following procedure was adopted. From 0.5 to 2 grams of the gel, previously heated for at least a half hour at 250°-300° in vacuo, was placed in a small bulb, which was then sealed to the stopcock and outer half of the ground-glass joint H, making the complete adsorption bulb I. The joint was lubricated with stopcock grease and fitted in place, and the system, including the bulb containing the gel, evacuated to a pressure of less than 0.001 mm. The stopcock of the bulb was then closed, and after equalizing pressure in the system, the bulb was detached, the lubricant on the joint removed with a clean cloth, and the bulb weighed.

Experiments were made to determine if the weight of the bulb, as determined in this way, was reproducible. The bulb was weighed, stopcock grease applied to the joint, then removed with a clean cloth, and the bulb re-weighed. A series of six such weighings agreed within 0.2 mg.

The bulb was placed in the calorimeter and again attached to the system, which was then evacuated, as before, to a pressure less than 0.001 mm. While the evacuation was in progress, sulfur dioxide was allowed to sweep out the drying train, connected to the system at E, the sulfur dioxide escaping at F. This drying train contained also an open manometer, in order better to regulate the admission of the gas. It was assumed that the air was completely displaced from the train between the tank and the stopcock D after sweeping the gas through at a moderate rate for half an hour. This was further checked by the time required for equilibrium to be established when the gas was adsorbed by the gel,—it having been shown by Patrick and McGavack that a pressure of air over the gel too small to materially affect the calculated pressure of sulfur dioxide would increase by several hours the time required for equilibrium to be attained.

Upon completion of the evacuation, the stopcock of the adsorption bulb was opened and the mercury reservoirs raised so as to close traps A and C. The calorimeter and adsorption bulb had come to thermal equilibrium at the end of the evacuation. The stopcock M, Fig. 2, was opened momentarily,

[1] J. Am. Chem. Soc. 42, 946 (1920).

allowing the capillary N to become completely filled with mercury, and a small weighed cup of mercury so placed that the tip of N was immersed in it. The stopcock D, Fig. 1, was then opened to the system for a few seconds, admitting a small amount of sulfur dioxide. During a run, a moderate current of sulfur dioxide was continuously passing through the stopcock D and out of the opening F, except when it was being admitted to the adsorption bulb.

The mercury cups used to determine the heat were changed every fifteen minutes until the weight was constant (within 0.5 mg.). Attainment of equilibrium was also followed by observing the pressure of gas over the gel, measured as the difference between the mercury levels in the two arms of the trap C, and read with a cathetometer telescope. It was observed that at lower pressures equilibrium was reached in fifteen minutes or less, and that if evacuation was properly carried out, it required in no case more than half an hour to establish itself.

When equilibrium was reached, as shown by both pressure and heat measurements, the total loss in weight of the mercury cups, and the pressure were recorded. The stopcock to the bulb was then closed and pressure equalized, whereupon the bulb was removed, dried and weighed. The increase in weight, corrected for the amount of sulfur dioxide in the free space of the bulb at the pressure observed, gave the weight of the sulfur dioxide adsorbed.

The bulb was then replaced in the calorimeter and again attached to the system, which was evacuated as before, the stopcock to the bulb being kept closed during the evacuation. When evacuation was complete the mercury traps were again closed, the stopcock to the bulb opened, and a second portion of gas admitted in the same manner. For the new pressure the heat of adsorption was recorded as the sum of the two heats measured, and the amount adsorbed is also taken as the total (corrected) increase in weight of the bulb, rather than the difference between two successive weighings.

In this manner four successive portions of gas were admitted, and the equilibrium pressures, total heat, and weight of substance adsorbed recorded for each point. The final pressure was never much greater than 600 mm., since if this pressure exists in the bulb at 0°, the pressure therein becomes greater than the external pressure when the bulb is allowed to come to room temperature.

After its final weighing, the bulb was attached to the system and evacuated In some cases it was first placed in the calorimeter and the heat of desorption measured. It was found that about 95 percent of the gas could be removed by evacuation at 0° for one hour. In any case, the evacuation was completed while heating the gel at 250°-300° for half an hour, after which the gel was ready for a second run. Several successive runs with the same sample of gel did not show any falling off in activity, the curves being practically coincident.

In the runs using water vapor, the method was, in general, the same. A bulb containing distilled water was sealed to the system at E. The water and the free space between the stopcock and the bulb containing the water were freed from air by repeated expansion into the remainder of the system, and were then kept air-free.

The time required for evacuation of the system was materially lowered by sweeping it out with water vapor by a suitable manipulation of the trap A and the stopcock D. Practically complete evacuation, except for water vapor, could be brought about in ten or fifteen minutes by this method. The stopcock to the adsorption bulb, which had been previously evacuated, was of course kept closed during this process.

A higher degree of evacuation was required for water vapor than for sulfur dioxide, in order that equilibrium might be established in the same time. The correction for water vapor in the free space of the bulb is negligible.

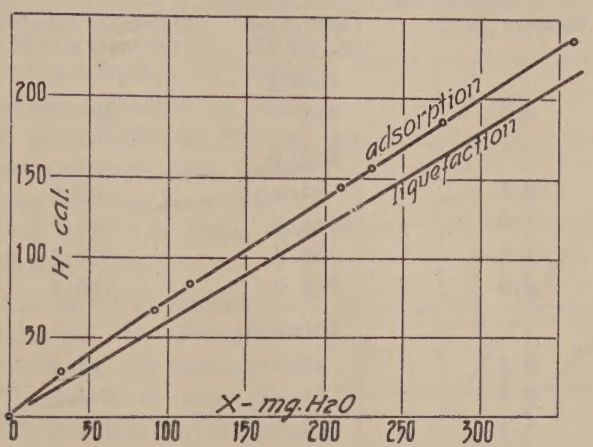

FIG. 3

Heat of Adsorption of Water Vapor at 0° C

Attempts to measure the heat of desorption were unsatisfactory, since only a small amount of water is removed from unit weight of gel on evacuation for one hour at 0°.

Discussion

The heat of adsorption of water vapor follows the upper curve of Fig. 3, which also shows the heat of liquefaction (vaporization) of water at 0°. The value of the latter is taken as 596.8 calories per gram, as measured by Dieterici[1]. The heat of adsorption is found to follow the equation $H = KX^{1/n}$ of Lamb and Coolidge, the values of K and 1/n being, respectively, 1.091 and 0.914. This is obtained from experiments 6 and 9 (Table I), which give partial heats of adsorption as well as the value at saturation. The other two runs give only the values at saturation of X and H. The mean weight of water adsorbed at saturation is 361.2 mg. per gram of gel, and the mean heat of adsorption at saturation is 236.2 calories per gram of gel. The heat of liquefaction at 0° of this weight for water is 215.6 calories, thus the net heat at saturation is 20.6 calories per gram of gel. The fact that this net heat is positive, while it

[1] Wied. Ann. **37**, 504 (1889).

does not preclude the possibility of compression of the adsorbed liquid by the forces of molecular attraction, makes it seem very improbable that this compression, if any, has any material effect on the heat of adsorption, since the compression of water at 0° would, according to the principle of LeChatelier, result in an absorption rather than an evolution of heat.

TABLE I

Heat of Adsorption—Water Vapor. 0°C.
Sample gel = 0.4568 gm.

Pressure (mm.)	Calories per gm. gel (H)	Milligrams adsorbed per gram gel (X)
	Run 4	
4.6	235	362
	Run 6	
0.8	66.4	90.8
1.6	143.9	210.1
3.4	184.4	276.5
4.6	233.0	359.2
	Run 9	
0.3	27.0	32.9
0.8	83.4	114.6
2.1	157.0	231.5
4.6	238.1	361.7
	Run 10	
4.6	237	362.0

The net heat may, however, be satisfactorily explained by a consideration of the changes in surface and in surface energy involved. As has been pointed out in a previous paper,[1] silica gel is assumed to have a water surface before wetting or adsorption, and the process of wetting or adsorption in the case of water simply consists in the filling of the pores of the gel, which reduces the original, very large surface to practically zero. The heat of wetting of silica gel by water as measured by Patrick and Grimm at 25° was 19.22 calories per gram of gel, while the net heat of adsorption of water vapor at 0° was shown by our measurements to be equal, at saturation, to 20.6 calories per gram of gel. The experimental error in the latter measurement is magnified considerably by the fact that the net heat, as is apparent from the curve, is less than one tenth of the total heat of adsorption as measured. It may be remarked in passing that in most of the cases observed by Lamb and Coolidge, the net heat was about one half of the total heat measured, and in our measurements of the heat of adsorption of sulfur dioxide on silica gel, shown below, the net heat also approaches this fraction of the total. That the heat of

[1] Patrick and Grimm: J. Am. Chem. Soc. 43, 2144 (1921).

wetting at 25° should be equal to the net heat of adsorption at saturation at 0° is evident when one considers the equation

$$\frac{E}{\omega} = \sigma - T\frac{d\sigma}{dT}.$$

According to this equation, since $d\sigma/dT$ is a constant and negative in value, E, the total surface energy of the liquid, between the above temperature limits, is practically constant.

The above measurements, then, provide further justification for the statement, previously made, that heats of wetting, or net heats of adsorption, can be explained satisfactorily by a consideration of the changes in surface energy involved.

The heats of adsorption of sulfur dioxide by silica gel, tabulated in Table II, are shown graphically in Fig. 4. These heat measurements also follow approximately the equation $H = KX^{1/n}$, the values of K and 1/n being, respectively, 0.316 and 0.860.

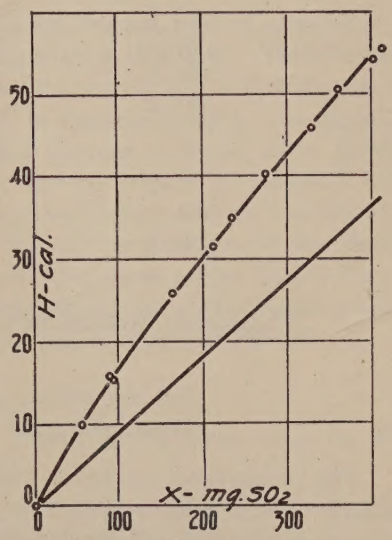

FIG. 4

Heat Adsorption of Sulfur Dioxide at 0°C

The adsorption of sulfur dioxide also follows the equation of Freundlich, $X = KP^{1/n}$, although the amount of sulfur dioxide adsorbed at any given pressure is slightly less than that observed at this temperature by Patrick and McGavack. This is undoubtedly due to slight differences in the structure of the different preparations of the gel. Inasmuch as the saturation pressure of sulfur dioxide in these experiments was in no case reached, our P — X curve (according to the Freundlich equation) was extended until P attained the saturation value at 0°. By this extrapolation, X attains the value 525 mg. per gm. gel. At saturation pressures, the volumes of all liquids held per gm. gel are, of course, equal. By substituting this value of X in the equation $H = KX^{1/n}$, one obtains a value of 69.1 calories per gm. gel for H,—which represents the heat of adsorption at saturation. Since the heat of vaporization at 0° of 525 mg. of sulfur dioxide is 47.9 cal., it follows that the net heat at saturation is 69.1 minus 47.9 or 21.2 cal. per gm.

The net heats of adsorption of sulfur dioxide were calculated also for the points measured, and it was found that they would follow approximately an equation of the form $H = KX^{1/n}$. The net heat of adsorption at saturation was extrapolated on this curve also, and a value was obtained of 21.4 calories per gram of gel, almost coincident with the value previously obtained.

TABLE II

Heat of Adsorption—Sulfur Dioxide at 0°.
Sample gel = 1.813 gm.

Pressure (mm.)	Calories per gm. gel (H)	Milligrams adsorbed per gram gel (X)
	Run 5	
11.8	15.5	94.8
78.7	31.4	213
290.0	45.8	330
577.5	54.2	405
	Run 7	
4.2	10.0	57.9
40.1	25.8	165
162.5	40.2	276
471.0	53.1	384
	Run 8	
10.7	16.0	90.8
102.5	34.8	236
388.8	50.6	360
611.2	55.8	416

Comparison Adsorption and Desorption Values (Run 5).

	Adsorption	Desorption
Cal. per gram	54.2	50.9
Mgms. per gram	405	369

The methods above used to obtain the net heat at saturation involve less chance of error than might at first be expected. The curve of the heat of adsorption, for instance, beyond the points measured, is approaching parallelism with the curve of the heat of liquefaction; so that the net heat,—the difference between these two values,—increases beyond the points measured rather slowly with increasing values of X. At the greatest measured value of X, the net heat is only 3 calories less than that calculated at saturation.

The saturation values for the net heat of adsorption of sulfur dioxide and of water vapor are thus seen to very nearly coincide,—the former exceeding the latter by less than one calorie. Since it is assumed that in the adsorption of water vapor the filling of the pores of the gel with water merely destroys the enormous water-air surface of the gel, reducing it to practically zero, it should follow in this case, that if the pores are filled with sulfur dioxide, the same water-air surface is destroyed, and the final liquid sulfur dioxide-air surface is as negligible as was the final water-air interface in the first instance. There is still the possibility, however, that the original water-air surface of the gel may now form a water-sulfur dioxide interface, with a certain positive or negative surface energy. This would be comparable to the wetting of silica gel by liquids not completely miscible with water, as observed by

Patrick and Grimm. In this case the net heat at saturation would vary from that observed in the case of water by the amount of total energy resident in this interface.

In most cases the total surface energy of an interface is positive, so that the heat of wetting of the gel by a liquid X would be less than that of pure water by the amount of energy resident in the interface water-X. However, cases have been observed in which a liquid-liquid interfacial tension has a positive temperature coefficient. In a case of this sort, although the free surface energy of the interface would of necessity be positive, it is conceivable that the total surface energy might be negative in sign, so that the heat of wetting, explained on this basis, would be greater in the case of a liquid exhibiting such a behavior with respect to water, than with water itself.

It is possible that the difference between the net heat of adsorption of water and of sulfur dioxide is to be explained upon this basis. There remains also, however, the possibility of reaction between the sulfur dioxide and the water already in the gel. It is stated in Gmelin-Kraut's "Anorganische Chemie" that water does not appreciably dissolve in liquid sulfur dioxide, except to form a hydrate. Most of the various possible hydrates of sulfur dioxide can exist at this temperature, but their heats of formation could not be obtained. It is possible, however, that the explanation of the slightly greater heat of adsorption at saturation in the case of sulfur dioxide than in the case of water is to be found in the formation of one of the various possible hydrates of sulfur dioxide by means of the water already in the gel.

Summary

1. The heats of adsorption of sulfur dioxide and of water vapor by silica gel have been measured at 0°.

2. Explanations, based upon surface energy considerations, have been advanced in both cases to account for the difference between the heat of adsorption and the heat of liquefaction; and possible causes of the difference between the net heats of adsorption of sulfur dioxide and of water have been discussed.

THE HEATS OF OXIDATION OF CARBON MONOXIDE AND OF HYDROGEN BY MANGANESE DIOXIDE AT 0°C*

BY J. C. W. FRAZER AND C. E. GREIDER

It has been shown by Frazer and Whitesell,[1] working in this laboratory, that manganese dioxide can be prepared in a form sufficiently active to powerfully catalyze the oxidation of carbon monoxide to dioxide in a dilute carbon monoxide-air mixture at 0° and below. These authors have further shown that when pure carbon monoxide is brought into contact with this active manganese dioxide, it is taken up by the catalyst and presumably either is adsorbed or reacts chemically with it. Whichever is the case, when attempt is made to remove the gas, only carbon dioxide results, the carbon monoxide being oxidized at the expense of the oxygen of the catalyst.

It was therefore decided to measure the heat attending this adsorption and oxidation, in the hope that it might throw some light on the mechanism of the reaction.

Apparatus and Materials

Except as noted below, the apparatus and the method of its operation were the same as has been illustrated and described by Patrick and Greider.[2] The source of carbon monoxide was a generator which permitted formic acid to drop sulphuric acid previously heated to any desired temperature, thus generating the gas as needed. The gas was purified by passage through a tube containing alternate layers of coarse and fine soda-lime. The generating flask and drying train, which contained also an open manometer in order better to regulate the admission of the gas, was sealed to the system at E, Fig. 1. The manganese dioxide was prepared from potassium permanganate and nitric acid as described by Frazer and Whitesell, pressed and dried at 150°-160° in vacuo. The source of hydrogen was a tank of the commercial compressed gas, which was freed of oxygen by passage through a U-tube filled with heated platinized asbestos, followed by a second U-tube filled with phosphorus pentoxide.

Procedure

Preliminary experiments with carbon monoxide showed that a large amount of heat was liberated during the admission of the gas to the manganese dioxide, indicating that the oxidation was practically immediate. Equilibrium was not attained at the end of several hours, however, due to the slow diffusion of carbon dioxide out of the adsorption or reaction bulb and of carbon monoxide into it.

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* Contribution from the Chemical Laboratory of Johns Hopkins University.

[1] J. Am. Chem. Soc. 45, 2841 (1923); also Whitesell: Dissertation, Johns Hopkins University (1923).

[2] J. Phys. Chem., 29, 1031 (1925).

The following procedure was therefore adopted. The system was evacuated as described in the preceding article, including the adsorption bulb, which contained one gram of pressed and dried manganese dioxide. The stopcock at H was then closed, pressure equalized, and the bulb detached and weighed. It was then placed in the calorimeter and attached to the system, which was re-evacuated, while at the same time the drying train was being swept out with carbon monoxide, which escaped at F. When evacuation was complete, the bulb had come to the temperature of the calorimeter, which was then made ready for a heat measurement.

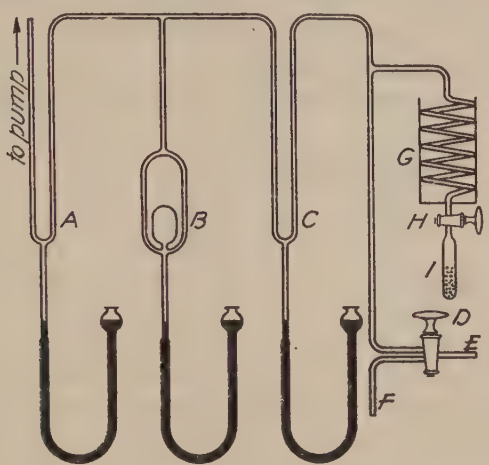

FIG. 1

The stopcock H was then opened and the stopcock D so turned that a slow current of carbon monoxide was admitted to the system. The rate of admission of the gas was so regulated that it required five minutes for the pressure to reach 650-700 mm. When this pressure was reached, the stopcock was closed and the three-way stopcock D so turned that carbon monoxide was no longer admitted to the system, in order to prevent diffusion to and from the adsorption or reaction bulb. Under these conditions thermal equilibrium was established in about half an hour. Measurements of equilibrium pressure could not be made by this method.

When no more heat was given off, the total heat was recorded, the stopcock to the bulb (H) was closed, the pressure equalized, and the bulb again detached, dried and weighed,—the increase in weight being recorded as carbon monoxide taken up. The bulb was then replaced in the calorimeter, and after it had acquired the temperature of the latter, it was attached to the system and evacuated for one hour, and the heat of desorption of the carbon dioxide measured. The bulb was then closed, the pressure equalized, and the bulb detached and weighed,—the loss in weight on evacuation being recorded as carbon dioxide removed, which included both that which had been adsorbed and that in the free space of the bulb. Calculation of the total loss in weight

as carbon dioxide necessitates the assumption that at equilibrium the carbon monoxide is practically completely oxidized, which is justified both by the observations of Whitesell, to which reference has already been made, and by the magnitude of the heat effect as measured.

At the end of the run, particles of manganese dioxide near the top of the bulb had changed from black to orange in color. When this sample is heated over night at 150° in a current of air, the orange color disappears. This treatment does not, however, restore the original activity of the sample, and a second run shows only about half of the amount of oxidation shown on the first run. A third run with the same sample after the same treatment shows still further falling off in activity. Heating in a current of oxygen is much more efficient in restoring the activity of the sample.

The results of the above measurements are recorded in Table I.

Measurements with Hydrogen

It had been observed in the dynamic method used by Whitesell that hydrogen in an air mixture was not catalytically oxidized by manganese dioxide at this temperature. It was thought that this might be due to poisoning of the catalyst by the water formed from the oxidation of the first portions of hydrogen admitted, since it is known that water poisons the catalyst for the oxidation of carbon monoxide. Runs were therefore made using hydrogen in place of carbon monoxide. The hydrogen was admitted to the system in the same manner as was the carbon monoxide, except that the stopcock H was left open after the hydrogen was admitted.

It was found that a slow but continuous fall in the pressure of the gas in contact with the catalyst took place. However, the heat given off at the end of an hour, as well as the increase in weight of the bulb, was negligible, indicating that the amount of water formed during this time had little if any effect on the catalyst.

TABLE I

Oxidation of Carbon Monoxide

	Sample III	Sample IV		
	Run 1	Run 1	Run 2	Run 3
Heat on admission of CO—calories	67.1	67.7	37.7	45.2
Heat on desorption of CO_2—calories	7.3	6.3	3.5	5.4
Millimols CO taken up	1.17	1.17	0.67	0.80
Millimols CO_2 removed	0.97	0.97	0.53	0.64

The fact that a slow but continuous fall in pressure of the gas in contact with the catalyst occurred, indicated that oxidation of the hydrogen was apparently taking place, but its slowness made it impracticable to follow the heat of the reaction. A bath of ice and water was therefore substituted for the calorimeter, and measurements made with the bulb immersed therein, no attempt being made to determine the heat of the reaction. Hydrogen was admitted to the system, the initial pressure read, and the change in pressure of hydrogen over the catalyst over a number of days was read and recorded, the results being given in Table II. The recorded temperatures are room temperatures, the bulb containing the manganese dioxide being kept at 0° throughout.

TABLE II

Oxidation of Hydrogen

Time hours	Pressure mm.	Temperature
0	612.7	25.7
3	596.2	26.0
19.5	560.5	24.3
27	555.7	25.5
50	537.2	25.8
70	529.0	26.3

Discussion

The work of Frazer and Whitesell, and of Patrick and Greider, already referred to, makes it seem very probable that carbon dioxide is rather easily desorbed from manganese dioxide at 0°. The observed decrease in weight of the bulb after evacuation for one hour did not, however, correspond to as much carbon dioxide as could have been formed from the carbon monoxide taken up. This might be explained by assuming the oxidation of the carbon monoxide to be incomplete, but this assumption agrees neither with the observations of Whitesell nor with the magnitude of the heat effect observed, which is shown below to be greater than that calculated on the assumption that all the carbon monoxide entering is oxidized.

It is assumed therefore that a portion of the manganese dioxide is reduced to MnO, which would with the CO_2 then form $MnCO_3$. This also accounts for the orange color shown by a portion of the catalyst after it is reduced It is assumed that for every mol of carbon dioxide pumped off a corresponding amount of manganese dioxide has been reduced to Mn_3O_4. It is further assumed that all the carbon monoxide entering is oxidized; therefore the number of mols of carbon monoxide undergoing the reaction

$$CO + MnO_2 \longrightarrow CO_2 + MnO \rightarrow MnCO_3$$

is the difference between the number of mols of CO entering and of CO_2 removed.

The heats attending these reactions were evaluated from the heats of formation,—the heat of adsorption of carbon dioxide being taken as numeri-

cally equal to its heat of desorption as measured. It should be noted that this heat of adsorption corresponds, not to the total amount of carbon dioxide removed, but to this minus the undetermined amount present in the free space of the bulb. It is possible also that some manganous carbonate is decomposed by the evacuation, since manganous carbonate probably has an appreciable carbon dioxide pressure even at this temperature.

All the heats of reaction corresponding to the weights of carbon monoxide and dioxide observed were summed up, together with the heat of adsorption of the carbon dioxide, and were compared with the total heat observed. These data are given in Table III.

TABLE III

Heat Data for Carbon Monoxide Oxidation

Reaction	Heat—cal.			
	Sample III	Sample IV		
	Run 1	Run 1	Run 2	Run 3
1	−7.0	−7.0	−4.9	−5.6
2	−23.2	−23.2	−12.7	−15.3
3	5.5	5.5	3.9	4.4
4	79.7	79.7	45.7	54.6
CO_2 adsorbed	7.3	6.3	3.5	5.4
Total heat calc.	62.3	61.3	35.5	43.5
Total heat obs.	67.1	67.7	37.7	45.2
Difference-percent	7.2	10.4	6.3	3.8

Reaction 1—$MnO_2 \longrightarrow MnO\ (+O)$
Reaction 2—$1\frac{1}{2}MnO_2 \longrightarrow \frac{1}{2}\ Mn_3O_4\ (+O)$
Reaction 3—$MnO + CO_2 \longrightarrow MnCO_3$
Reaction 4—$CO\ (+O) \longrightarrow CO_2$

The results given by Sample IV, Table III, indicate that when the catalyst is reduced with pure carbon monoxide it is reoxidized with considerable difficulty. After the first run the sample was heated over night in a current of dry air, as described under "Procedure". Its oxidizing power on the second run, after this treatment, was only about half of that shown on the first run, indicating that it had not been completely reoxidized. It was then heated over night at the same temperature—150°-160°—in a current of oxygen. The third run, after this treatment, showed a greater oxidizing power than the second, the extent of the oxidation being about two thirds of the value obtained on the first run. Continued heating in a current of oxygen should therefore completely restore the activity of the sample, by completing the reoxidation of the catalyst.

Calculations were made to see if the change in pressure of hydrogen over the catalyst, Table II, was proportional to either the pressure or the square

of the pressure of the hydrogen over the sample. Values of K for different values of t were obtained for the equations

$$-\frac{dP}{dt} = KP$$

$$-\frac{dP}{dt} = KP^2$$

In either case the values of K fell off considerably with increasing values of T. In case the reaction had been proportional to the amount of hydrogen adsorbed by the catalyst, K as calculated would have increased with increasing time and decreasing pressure, since the ratio of the amount of a gas adsorbed to the pressure increases as the pressure decreases. In other words, the adsorption is relatively greater at lower pressure.

The decrease in value of K with increasing time is probably due to changes in surface of the catalyst, brought about by the slow oxidation of the hydrogen, which cause the reaction rate to decrease.

Summary

1. The oxidation of carbon monoxide and of hydrogen by active manganese dioxide has been studied, and the heat of the former reaction has been measured.

2. A mechanism has been proposed for the oxidation in the case of carbon monoxide.

BIOGRAPHY

Clarence Edwin Greider, the author of this dissertation, was born in Lawrence, Kansas, on the 25th day of February in the year 1899. He received his elementary and secondary school education in the public schools of Topeka, Kansas. He graduated from Washburn College, of the same city, in 1920, receiving the degree of Bachelor of Science. He received the degree of Master of Science in Chemistry from the State University of Iowa in August, 1921. In September of that year he enrolled himself as a student in the department of chemistry of the Johns Hopkins University. In the same year he married Miss M. Cornelia Widney of Chambersburg, Pa. He is a member of Tau Delta Pi (honorary scholastic) of Washburn College, the American Association for the Advancement of Science, and Gamma Sigma Epsilon (honorary chemical).